Liquid-phase adsorption: common problems and how we could do better

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Abstract

Adsorption plays a vital role in many applications from adsorbents for concentrating valuable compounds or removing pollutants to catalysts. In gas and liquid phases, the adsorption phenomena may look similar and the results are often transferred. But solvents play a role and may change the adsorption behaviour even for strong adsorbates – liquid phase adsorption is different!

The review covers kinetics and thermodynamics of adsorption processes and focuses on several areas that receive only minor attention despite being crucial for obtaining reliable results. Such underappreciated areas include the analysis of how to maximise experimental accuracy of adsorption studies and analyse the model parameters and their confidence intervals; the effect of the mathematical representation and model linearization on the results; the possibility of processes other than adsorption during the experiments.

The experiments based on disappearance of the adsorbate from the equilibrium solution shall be performed to ensure at least 10% decrease in concentration for reasonable accuracy. Regression analysis and analysis of the confidence intervals of the parameters merit particular attention as well as an independent validation of the model assumptions. Even an excellent data fit may provide results differing by several times from the correct values.

Adding to the dispute on dimensions in the adsorption constants in van't Hoof equation, the review adds arguments in favour of using constants in L/mol units. The review concludes with the proposed workflow in the analysis of liquid-phase adsorption data from the data acquisition to data analysis and modelling and offers a Matlab app for Langmuir adsorption data analysis.

Keywords: adsorption; error; Langmuir; catalysis; Equilibrium constant; adsorption kinetics

1. Introduction

In the United Kingdom as an example, chemicals constitute the 3rd largest manufacturing sector that employs 400,000 people and generates £48.7bn turnover [1]. The chemicals manufacturing relies on catalytic processes, mainly heterogeneous catalysis, judging by the value and scale of the production [2,3]. There is barely a synthesis that does not include a catalytic step – from petroleum cracking into fuels to the synthesis of cancer drug candidates [4–6]. Adsorption extends far beyond catalysis being vital in pollution removal, in concentrating of rare compounds. Aqueous effluents from most industries such as paint, pesticide, petroleum, printing, pharmaceutics, wood, paper, steel, textile contain chemicals are treated by adsorption processes [7].

Adsorption of substrates on the catalyst surface is one of the key reaction steps - the steps critical for the catalyst performance but all too often overlooked. Adsorption energy must fall within a narrow range to provide the highest reaction rate – too strong adsorption hinders reaction creating catalyst surface overly occupied with the substrate, too weak interaction provides low catalyst coverage and low probability of the reaction. This Sabatier principle is one of the key findings in catalysis – the corresponding volcano plots (reaction rate versus adsorption energy) are observed in all the areas of catalysis [8–10]. Complex reaction networks with multiple intermediates and bond formations could be accurately described only in terms of a single desorption process [11]. On the other hand, the adsorption phenomena are sometimes detrimental for catalysis – strong adsorption of by-products is often the cause for catalyst deactivation [12–15]. Hence, understanding of the adsorption processes is vital for the catalyst design.

The adsorption process itself, however, is scarcely studied directly in liquid-phase reactions. The insights are often obtained only indirectly using kinetic modelling or DFT computation. Data generated in gas-phase is often transferred into the liquid phase. This approach seems reasonable especially for non-reactive solvents and strong adsorbates. However, such a common sense does not always hold. For example, Pt nanoparticles encapsulated with polymer dendrimers show drastically different behaviour in solvents compared to gas-phase even for carbon monoxide [16]. In gas phase, the particles adsorb carbon monoxide weakly with low capacity; in liquid-phase, both the capacity and adsorption energy increase because the dendrimer polymer swells and opens the catalyst surface [16]. Considering that such a dramatic effect was observed for one of the strongest adsorbates, the validity of a casual transfer of results from gas phase into the liquid phase becomes questionable.

The study of liquid-phase adsorption in catalysts differs from conventional adsorbates, and this difference may bring insights into the conventional adsorption. Conventionally, the dyes,

heavy metals or environmental pollutants in low concentration are adsorbed over active carbons or natural materials [7,17–20]. By their design and intended application, these adsorbents must have a high adsorption capacity with high adsorption constant. For catalysts, in contrast, the Sabatier principle limits the adsorption constant. Moreover, the supported catalysts with a few percent of the active component have a much lower adsorption capacity. Both the lower constant and capacity make the adsorption studies much more challenging and demanding. Such demands, however, surface many critical aspects of the adsorption studies; therefore, the insights and conclusions derived will be of value for all aspects of the liquid phase adsorption.

Understanding the adsorption processes with direct studies in liquid phase could open ways for a deeper understanding of the reaction mechanisms and development of more selective and efficient catalysts. This review discusses the main adsorption models and potential problems which attract little attention but can have drastic implications on the results obtained.

2. Experiments on liquid-phase adsorption

The adsorption experiments are generally based on the material balance. An adsorbent material is exposed to the adsorbate solution with a known concentration. The adsorbate concentration decreases in the solution ($V_{solution}$) and adsorption (q_e) is calculated as the difference between its introduced ($C_{initial}$) and the remaining concentrations ($C_{equilibrium}$) based on the equation 1. Adsorption is often normalised by the adsorbent mass.

$$q_e = V_{solution}(C_{initial} - C_{equilibrium}). \quad (1)$$

This approach is widely used in the analysis of dyes or metal ions [17,21–24] as well as for the catalytic applications [25]. Obviously, this material balance approach is simple, however, there are several problems that the reader must be aware of.

The first problem with the approach is the possibility of unforeseen interactions. These may include chemical reactions, reactions with the impurities, and the effect of the adsorbent on the medium. For example, the adsorption of Cr(VI) brought in contact with an adsorbent may lead to reduction in addition to adsorption. Species of Cr(VI) may react with the surface to form Cr(III) and be desorbed [26]. As a result of Cr(III) desorption, the Cr(VI) content in the solution decreases. In the case of photometric analysis of Cr(VI) concentration, a strong decrease will be observed that may be wrongly attributed to high adsorption. Hence to avoid such problems, a possibility of such reactions as well as alternative analysis methods shall be considered.

The second problem comes from using the concentration difference in equation 1 which may dramatically increase measurement errors. Equation 2 shows the error in the adsorption determined with the experimental errors denoted with symbol δ:

$$\delta q_e = |q_e| \sqrt{\frac{\delta V^2}{V^2} + \frac{\delta C_{initial}^2 + \delta C_{equilibrium}^2}{(C_{initial} - C_{equilibrium})^2}} \,. \qquad 2$$

The second term under the square root shows that the error in the adsorption increases when the *relative change* in concentration is small. This conclusion is intuitive – analysis of small changes against a large background is difficult.

The analytical error (in concentration) is often proportional to the determined value ($\delta C = \xi \cdot C$) when concentration is far from their detection limits [27,28]. Neglecting errors in volume measurement, the relative error in adsorption may be simplified as shown in equation 3:

$$\frac{\delta q_e}{|q_e|} = \xi \frac{\sqrt{C_{initial}^2 + C_{equilibrium}^2}}{|C_{initial} - C_{equilibrium}|} = \xi \sqrt{1 - \frac{2}{\Delta C_{relative}} + \frac{2}{\Delta C_{relative}^2}} \,, \qquad 3$$

where $\Delta C_{relative} = \frac{C_{initial} - C_{equilibrium}}{C_{initial}}$.

Fig. 1 shows that the error in the adsorption analysis is affected by the *relative* decrease in concentration. If the relative change in concentration is small (<0.05), the error in adsorption dramatically increases rendering results unreliable. A relative change in concentration, however, depends on both the intrinsic adsorption properties and on the amounts and concentrations used.

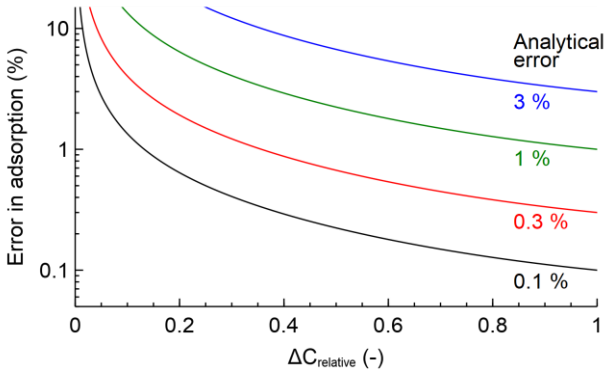


Fig. 1. The relative adsorption error as a function of analytical error and the relative change in adsorbate concentration; the analysis is based on the material balance approach (equation 1).

The error analysis shows that there is a limit on the concentration range that could result in accurate experimental results on adsorption. Moreover, excellent analytical reproducibility is important being a limiting factor in adsorption accuracy.

Considering limitations in the material balance approach, an alternative method of directly analysing the amount of material adsorbed seems particularly promising. Such a method means detecting the adsorbed material directly on the adsorbent. In case of gas phase, such studies are somewhat easy considering an absence of solvent and the possibility for direct spectroscopic and even gravimetric analyses. Examples include titration of acid sides of zeolite materials with nitrogen bases and observing a decrease in acidic groups in the spectra or appearance of new bands [29,30]. These methods, however, are fraught with their own issues and uncertainties [31]. (Spectroscopic studies require knowledge of molar absorption coefficients which may change with coverage). Another way of studying the amount adsorbed may be desorption experiments performed, for example, carrying out solvent exchange [32] or temperature-programmed desorption [33].

The material balance experiments may over-estimate adsorption because of unforeseen reactions between the adsorbate and the material; the desorption experiments under-estimate in case of dissociative or strong adsorption. Therefore, all studies require attention and care. Independent data validation such as a combination of both adsorption and desorption or a combination of spectroscopy with gravimetry is a good way to minimise the uncertainty [34].

3. Adsorption isotherms and data analysis

Once the adsorption data are obtained over a range of equilibrium concentrations, these are conventionally presented and analysed in terms of adsorption isotherms. There are many models that vary in physical meaning, the number of parameters and the accuracy of the description. Here, several widely used adsorption isotherm models are presented and more details could be found in reviews by Tran et al. or Rangabhashiyam et al. [17,26].

The Langmuir model is omnipresent because of simplicity and obvious physical meaning of the parameters. Equation 4 shows the relationship between the adsorption at equilibrium concentration $C_{equilibrium}$, adsorption constant K_L, and maximum adsorption capacity of $q_{\max}$:

$$q_e = q_{\max} \frac{K_L C_{equilibrium}}{1 + K_L C_{equilibrium}} \quad . \qquad 4$$

The Langmuir model assumes that the adsorbent surface is uniform – it contains a fixed number of sites that demonstrate identical adsorption energy, the adsorbant molecules could adsorb reversibly only over unoccupied sites, and do not interact with each other.

Another widely used Freundlich isotherm is shown in equation 5:

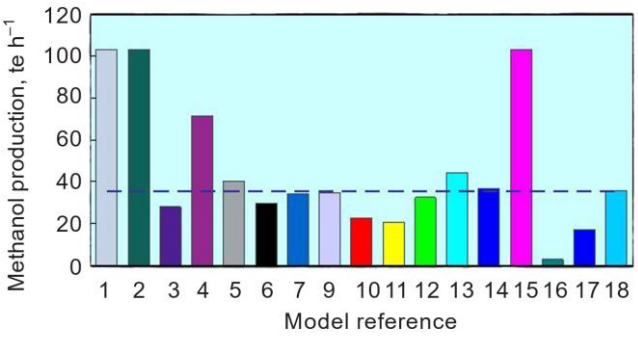
$$q_e = K_F C_{equilibrium}^n, \qquad 5$$

where K_F is the adsorption constant and *n* is the empirical parameter. This model is empirical; it often correctly describes adsorption over non-uniform surfaces but not the saturation behaviour.

In performing a regression analysis of the experimental data, there are two potentially conflicting aims: (i) to describe the system behaviour, or (ii) to gain mechanistic insights. The mechanistic aim, obviously, requires rigour in the data analysis and independent validation of the model assumptions. The descriptive aim seems deceptively simple. But the descriptive models are often extrapolated beyond the studied range of parameters. In this case, a careful analysis of the model and the data obtained becomes vital.

Correlation does not mean causation – people with umbrellas, although strongly correlating, do not cause rain. A computationally accurate description of a particular isotherm (good fit) does not show that the model is correct [31]. The model assumptions might not be fulfilled resulting in unexpected behaviour beyond the studied range. Even if the model is correct, the parameters obtained may be inaccurate resulting in unreliable extrapolations. Stitt at al. [35] writes: “Just because the results are in colour, it doesn’t mean they are right” and provides ample examples of totally inaccurate yet computationally valid model descriptions.

A minor mistake in the model may lead to dramatic changes in the extrapolated results [35]. The example in Fig. 2 shows the results of kinetic modelling of the same data with various models. All of these models showed an excellent fit with the R^2 values above 95%, most above 99%. The dashed line shows the “correct” data possible because the fitted data were artificially generated from a known kinetic model. Despite an excellent fit in all the models, the results are dramatically different - as much as 350% different!



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172 Fig. 2. The discrepancy in various kinetic models of the artificially generated kinetic data
173 (dashed line). Reprinted from ref. [35] which is based on the data obtained from ref. [36].

174

175 To avoid such poor results as in Fig. 2, the model must be validated by varying other
176 parameters such as temperature/pressure dependence. In the case of gas-phase
177 adsorption, Malek and Farooq [24] studied several models and compared the temperature
178 behaviour and accuracy in describing the competitive adsorption. But the first step in
179 assessing the model is to perform curve fitting and ensure that the parameters are well
180 defined.

181 The confidence intervals are most often estimated using black-box computational packages
182 that provide totally misleading data especially for non-linear models such as Langmuir
183 isotherm. A conventionally used linearization approach, on the other hand, introduces
184 additional errors and affects error estimates by imposing co-variation between parameters.
185 Bolster and Hornberger [37] discuss that Langmuir linearization may lead even to
186 computationally inaccurate results. A dramatic example is presented by Hamdaoui [38] who
187 applied two Langmuir linearization methods to the experimental data and obtained
188 dramatically different parameters. The differences between the Langmuir parameters
189 obtained with 2 models ranged between -85% to +27%, while the goodness of fit was above
190 98.5% in both cases. Goodness of fit is not sufficient!

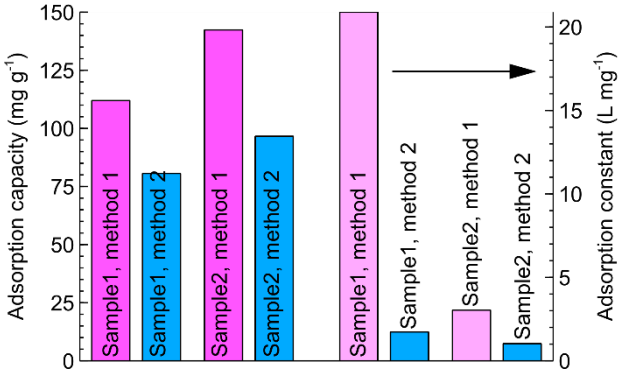

Fig. 3. Parameters of a Langmuir isotherm fitted with two linearization methods for two samples. The figure is based on the data by Hamdaoui [38].

Supplementary SI2 takes adsorption parameters from ref. [39], generates sets of model datapoints with an introduced normally-distributed error and performs regression analysis using various methods. Not surprisingly, the results show that the non-linear Langmuir approach with proper error weighing (discussed below) provide results closest to the correct adsorption parameters. Disregarding error weights creates almost twice larger deviations from the correct values, while linearization methods often produce unreliable data.

Proper curve fitting. The regression analysis has to be done properly as the example in Fig. 3 demonstrates. The first step is to avoid linearization and use non-linear model equation combined with the estimated experimental analytical errors. That may sound difficult but proper regression is simple – it minimises the objective function (weighed residual) as shown in equation 6:

$$f_{objective} = \sum_i \omega_i (q_{experiment,i} - q(C_i))^2 \,, \qquad 6$$

where $q_{experiment,i}$ are experimental adsorption datapoints, $q(C_i)$ the model values, and ω_i are the statistical weights of the *i*-th point. It is the weighing factor that makes a difference.

The weighting factors are calculated from the expected analytical uncertainties using equation 7, where σ_i is the uncertainty (standard deviation) in the analysis of datapoint *i*, and ξ_i is the relative experimental error (typically 0.5 – 2 % = 0.005 – 0.02). A more general case of errors both in X and Y axes is shown in Supplementary SI1.

$$\omega_i = 1/\sigma_i^2 = 1/(\xi_i q_{experiment,i}(C_i))^2 \qquad 7$$

Considering that in most cases, the *relative* experimental errors are constant (except when close to the detection limit) [27,28], the objective function could be simplified as in equation 8 :

$$f'_{objective} = \sum_i (1 - \frac{q(C_i)}{q_{experiment,i}})^2 . \quad (8)$$

Performing regression in most of the software packages (Origin, Excel) would result in the implicit assumption of constant *absolute* errors (rather than relative ones). As a result, high concentrations (with the corresponding high absolute errors) will be disproportionally well fitted and low concentrations may be, in effect, neglected. This approach of constant absolute errors combined with non-linear model may lead to worse results compared to unpredictable linearized approaches. The most reliable approach, however, is to use non-linear model with the objective function in equation 8. Supplementary SI2 elaborates on the inaccuracy of linearization models.

Confidence intervals. Once a proper curve fitting is performed, the next step is to study the confidence intervals. Likely the simplest and the most reliable way to perform such an analysis is to use the Monte-Carlo method described by Alper and Gelb [40] – the method that automatically accounts for co-variation in the model parameters. Many software packages generate some estimations on the confidence intervals but these may be grossly inaccurate [40].

The idea of the Monte-Carlo method is to generate a number (100-1000) of mock fitting data (experimental data plus random noise with the experimental standard deviation). These mock data are fitted and generate a set of model parameters. The statistics of the parameters obtained show the confidence intervals.

Broad confidence intervals show that the values cannot be relied upon and the model likely contains too many parameters. The widely used adsorption models contain only two parameters, but there are many models with as much as 5 parameters [24,26,41]. A larger number of parameters improves goodness of fit but makes all the parameters far less defined.

4. Analysing thermodynamic parameters

Any spontaneous process occurs because the system moves toward the minimum of the Gibbs's free energy, ΔG^o_{ads} in equation 9. Considering that the adsorbate molecules move from the 3-dimentional freedom of the solution onto a 2-dimensional catalyst surface, the adsorption entropy (ΔS^o_{ads}) often decreases. In this case, the adsorption enthalpy (ΔH^o_{ads}) must be negative for the adsorption to take place.

$$\Delta G^o_{ads} = \Delta H^o_{ads} - T\Delta S^o_{ads} . \quad (9)$$

The thermodynamic parameters of the adsorption are often obtained from the relation between the adsorption constant ($K_{equilibrium}$ in L mol^{-1}) and the Gibbs free adsorption energy (van't Hoff equation) 10. Here R is the universal gas constant and T is the adsorption temperature. The adsorption constant here could be either Langmuir of Freundlich constants in case of diluted solutions. More details on the ways to obtain the constant suitable for this equation are provided in reviews [42,43].

$$\Delta G^{o}_{ads} = -RT \ln K_{equilibrium} \qquad 10$$

The problem of the dimensioned constant. The Gibbs standard energy has dimensions of J mol^{-1}, the same as these of *RT. Hence,* the logarithm and the constant is dimensionless.

There is a controversy in how to resolve the misalignment of dimensions – $K_{equlibrium}$ must be dimensionless but the measured constant has the inverse units of concentration. There is a flurry of recent papers on the topic which argue on how to reconcile this problem of dimensions. First of all, both sides agree that the units of measured adsorption constant must be recalculated into L mol^{-1}, rather than keeping more exotic units such as mg g^{-1}. Such a simple matter is sometimes overlooked rendering results incorrect [26,42,44].

There is a hot disagreement, however, on the ways how to convert the dimensioned into the dimensionless constant. The problem comes from the value of the equilibrium adsorption constant shown in equation 11:

$$K_{experimental} = \frac{\alpha_{A\_adsorbed}}{\alpha_{A\_in\_solution}\,\alpha_{adsorbent}}. \qquad 11$$

Here $K_{experimental}$ is the adsorption constant and α are the activities of the corresponding species: adsorbed compound A, compound A remaining in the solution at equilibrium, and the adsorbent itself. The equation could be simplified considering activity coefficients 1 (which is valid for non-ionic and diluted ionic solutions [42,45]) and considering the Langmuir model the equilibrium coverage of θ. The resulting equation 12 shows the origin of the dispute – the constant determined experimentally has units of inverse concentration.

$$K_{experimental} = \frac{\theta}{C_{A\_in\_solution}(1-\theta)}. \qquad 12$$

Both sides of the dispute agree that the problem shall be resolved by multiplying the experimental constant (in L mol^{-1}) by a certain coefficient (in mol L^{-1}) that renders the product dimensionless. The value of the coefficient is disputed.

On one side, Milonjić [46] and Tran et al. [26,45] suggests multiplication by 55.5 mol L^{-1}. This constant is a concentration of water in the solution. Zhou and Zhou [45] provide a detailed proposition explaining that the constant of 55 mol L^{-1} comes from considering adsorption competition between the adsorbate and the solvent.

On the opposite side, Liu [47], Ghosal and Gupta [42] provide reasons that the constants shall be multiplied by 1 mol L^{-1}. The reasoning comes from the description of thermodynamic constants in terms of activities, not concentrations. The activity of component A is shown in equation 13:

$$\alpha_A = \gamma_A \frac{C_A}{C_{ref}}, \qquad 13$$

where γ_A is the activity coefficient, C_A is the concentration of the adsorbed specie in mol L^{-1}, and C_{ref} is the concentration of the reference state equal to 1 mol L^{-1} [42].

The reader is advised to read papers from both sides of the argument (in particular papers by Ghosal and Gupta [42], and Zhou and Zhou [45]) to form a coherent picture. In the current review the author, however, offers additional reasoning that may clarify the dispute. There are two points that both lead to the same conclusion on resolving the dispute.

The first point is that the same problem of dimensioned adsorption constants shown in equation 12 equally applies to gas phase, but there is no disagreement there. The gas-phase adsorbate concentrations may be presented in the units of in mol L^{-1}, or even mol mol^{-1} (molar fraction of adsorbate in gas phase). More conventionally, however, pressure is used as a measure of adsorbate activity rendering the corresponding experimental constant in bar^{-1}. This difference between the gas and liquid phases, however, shows that rendering the *concentration itself* dimensionless (using mole fraction) makes little sense. In liquid phase, multiplication of the constant by 55.5 mol L^{-1} renders, in effect, concentrations dimensionless molar fractions. The reason is that using mole fractions does not explain the increasing adsorption at a higher pressure. If we double pressure, we expect higher adsorption. If we consider molar fraction (that is 1 regardless of pressure) we would struggle explaining the difference in adsorption. Hence, the experimentally determined adsorption constant must be dimensioned in gas and liquid phases.

The second point comes from the analysis of how the problem of dimensioned constants could affect the resulting Gibbs energy assuming for the argument's sake the possibility of logarithmic Joule as a physical unit. Equation 14 explicitly states the constant ϑ required to make the experimental constant dimensionless:

$$\Delta G^{o}_{ads} = -RT \ln (\vartheta K_{experimental}) = -RT \ln \vartheta - RT \ln K_{experimental} . \quad (14)$$

Considering the arithmetic of logarithms, equation 14 shows that such constant ϑ simply provides an offset to the determined Gibbs energy of $-RT \ln \vartheta$. The corresponding offset affects the absolute value of the Gibbs energy we observe. Considering equation 9, this offset translates to an offset in the value of the adsorption enthalpy but does not affect the adsorption entropy which depends on the slope in the *G* vs *T* plot.

This consideration implies that the absolute value of the Gibbs energy, as well as enthalpy, cannot be determined, while that of entropy could be. Such a trivial statement, unsurprisingly, agrees with thermodynamics – the existence of absolute values of entropy and only relative values of enthalpy. For simplicity, enthalpy is often referred to certain reference states as elements stable under normal temperature and pressure.

The standard conditions for gases, defined by IUPAC, are the temperature of 0 ^{o}C and a pressure of 1 bar. Hence, all gas-phase adsorption constants are calculated in terms of bar^{-1} with the (often implied) "dimensionalisation" constant ϑ of 1 bar [48]. In liquid phase, the standard IUPAC state is for a solute at a concentration of 1 mol dm^{-3} rendering the required "dimensionalisation" constant ϑ of 1 dm^3 mol^{-1} [48]. Therefore, the correct way of calculating the thermodynamic parameters from the liquid-phase adsorption data is shown in equation 15:

$$\Delta G^{o}_{ads} = -RT \ln (K_{experimental}[in\ L\ mol^{-1}\ \ for\ diluted\ solutions]). \quad (15)$$

Analysis of adsorption thermodynamics. If the Gibbs adsorption energy obtained is negative, the adsorption is often said to occur "spontaneously" [26,41,42,44,46]. However, the "spontaneous" does not mean "occur". A small but negative value of the Gibbs free energy shows that the equilibrium constant is below 1 (equation 10). This note may be of little practical value for the design of pollutant adsorbents that must strongly adsorb to be useful. For the catalytic applications, however, both too high and too low adsorption constants are obstacles for the reaction. An "optimal" adsorption constant (that provides the highest reaction rate) might be below 1, the Gibbs adsorption energy may conceivably be positive.

Having the Gibbs adsorption energy determined, the adsorption enthalpy and entropy may be obtained using equation 9 by studying adsorption at various temperatures. Such a derivation, albeit trivial, raises an interesting question of correlation between the parameters derived. Anastopoulos and Kyzas in their review [44] show a strong correlation between the thermodynamic parameters obtained in the literature (Fig. 4) and call for alternative and independent ways to validate the parameters.

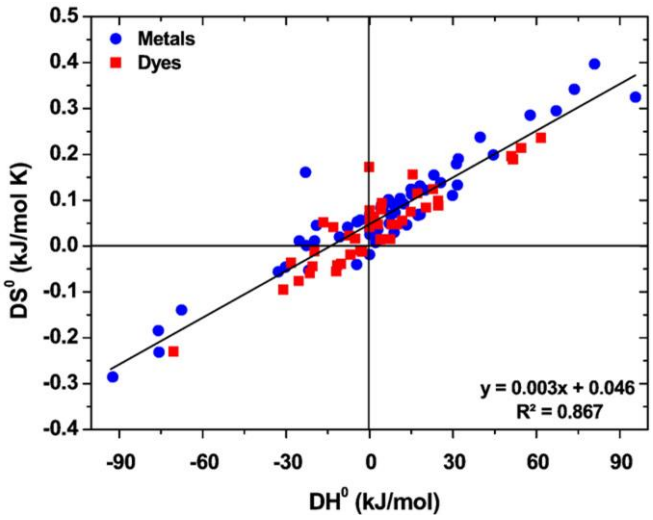

Fig. 4. Correlation between the adsorption entropy and enthalpy observed for the dyes and metal ions over various materials. The picture is reprinted from review [44].

The observed values of adsorption entropies and enthalpies can fall into 4 major groups depending on if they are positive or negative. Fig. 4 shows that the more prevalent are cases with exothermic adsorption with a negative adsorption enthalpy; and endothermic reactions with the increasing entropy. However, all the cases are realised in the literature [41]

5. Adsorption kinetics

The adsorption kinetics are often studied using similar approaches as thermodynamics; the only difference is the analysis in the adsorbate concentration change over time. The data obtained are fitted to a model. Similarly to thermodynamics, fitting shall benefit from using non-linearized equation to account for changing *absolute* experimental errors (and often constant *relative* experimental errors). (Equation 8 provides the way to calculate fitting residuals in such a case). The uncertainty intervals of the model parameters obtained shall be checked using Monte-Carlo.

A particular consideration for kinetics is the required analysis duration. Fig. 5 shows computer-generated adsorption data based on pseudo-second order kinetics with the analytical uncertainty of 3% (Supplementary SI3). Once the equilibrium is reached, the concentration does not change and the data points characterise the adsorption thermodynamics, not kinetics. Hence, taking too many of these points into regression may introduce unnecessary errors into the parameters determined; in the best case, these points are valueless.

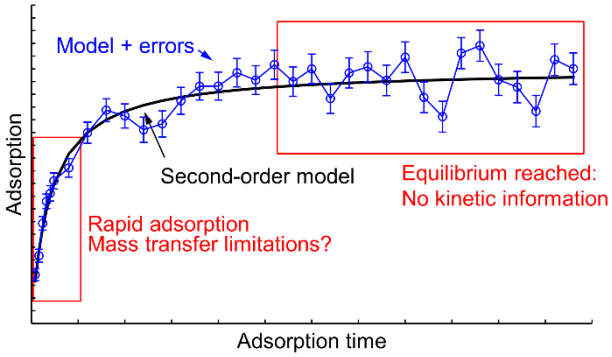

Fig. 5. Computer-generated data for pseudo-second order adsorption model with an experimental error at 3% (standard deviation) analytical uncertainty. The initial region may be limited by mass transfer; the equilibrium region contains no kinetic information.

While analysing adsorption kinetics, similar to reaction kinetics, one needs to study if the external mass transfer is not the rate-limiting factor. Otherwise, the data will reflect the rate of stirring rather than intrinsic adsorption. A simple way to check for external mass transfer is to perform experiments at various stirring rates and observe rates of adsorption constant above a certain stirring rate. However, many small reactors show minor changes in the Reynolds number in a broad stirring rate and may provide misleading results [49]; too high rotation rate, however, may decrease mass transfer [50]. Hence, a comparison of smaller and larger stirrers, possibly impellers, may be carried out for the test [51].

Internal mass transfer – the diffusion of the adsorbate molecules into the pores may often be a rate-limiting factor. In this case, the researcher may either look for the intrinsic rates of adsorption that requires studies with smaller adsorbent particles or using wall coatings [14,52,53]. Often, however, it is more practically important to characterise the apparent rates – in effect, internal mass transfer because such data characterises the behaviour of the adsorbents in many practical applications. The examples include adsorption of metal ions and dyes over chitosan (lobster shell waste) [21] and similar agricultural waste materials that have low porosity [32,54].

There are 3 most widely models used for describing the adsorption kinetics: pseudo first or second order, and internal diffusion. A wider range of adsorption models and equations are discussed by Qiu et al. [54].

Pseudo first or second order models treat adsorption in terms of a corresponding order chemical reaction with rate equations shown in equations 16 and 17:

$$\frac{dq(t)}{dt} = k_1(q_{equilibrium} - q(t)); q(t) = q_{equilibrium}(1 - \exp(-k_1 t)), \quad 16$$

$$\frac{dq(t)}{dt} = k_2(q_{equilibrium} - q(t))^2; q(t) = \frac{q_{equilibrium}^2 k_2 t}{q_{equilibrium} k_2 t + 1}, \quad 17$$

where k are apparent adsorption rate constants, $q(t)$ is the adsorption at the moment of t and $q_{equilibrium}$ is the equilibrium adsorption. These equations are often linearized, which as discussed above, may introduce unpredictable errors into the parameters obtained by regression (Fig. 3).

The other commonly used model considers intra-particle diffusion as the rate-limiting step. The adsorbent is considered homogeneous spheres with the mass transfer determined by equation 18 [54,55]:

$$\frac{\partial q(t,r)}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}(r^2 \frac{\partial q(t,r)}{\partial r}), \quad 18$$

where q is the adsorption at the moment t and radial position in the particle r, D_s is the intra-particle diffusion coefficient. This equation could be solved and simplified to obtain equation 19:

$$q(t) = q_{equilibrium} \cdot 6\sqrt{\frac{D_s}{\pi R^2}}\sqrt{t}, \quad 19$$

where $q_{equilibrium}$ is the equilibrium adsorption and R is the particle radius. Such an approximation is valid for $q(t)/q_{equilibrium}$ < 0.3 [54,55].

6. Conclusions

The review discusses experimental approaches, modelling to obtain thermodynamic, and kinetic parameters of adsorption. The suggested workflow is schematically presented in Fig. 6.

The planning steps involve assuming or estimating the adsorption constant; calculating the adsorbent mass and adsorbate concentrations to ensure that the measured adsorption could provide the desired accuracy. Reasonable accuracy is expected if the initial concentration changes by at least 10% relative to the initial concentration; otherwise the experimental errors would make results unusable (Fig. 1).

The experiment steps involve adsorption measurements and assessing the data with alternative methods to exclude the possibility of false readings caused by side-phenomena other than adsorption. An always advisable sanity check may involve comparing the

adsorption data with the known properties of the material such as overall surface area or adsorption site stoichiometry.

The modelling steps include selecting the adsorption model, curve fitting of the experimental data using the original non-linear equations, and considering experimental errors. The fitting objective function may be the one shown in equation 8 – the function that assumes constant relative errors in adsorption and no errors in the X axis values. Confidence intervals of the model parameters shall be calculated for mathematical sanity of the model using the Monte-Carlo approach [40]. Linearized models provide less predictable and often outright inaccurate results as shown in Supplementary SI2. Such calculations may be performed using the Matlab code for the Langmuir model; a standalone executable freely available at ref. [56].

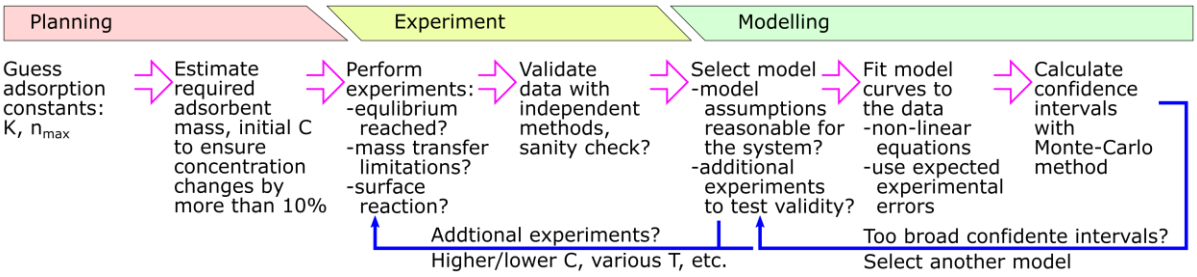

Fig. 6. Proposed workflow for adsorption experiments and analysis.

These steps allow obtaining mathematically reasonable results and assess the goodness of fit for the model selected. However, a good fit of the model and narrow confidence intervals do not validate the underlying model assumptions. If the modelling aims to probe into the adsorption mechanisms, the model assumptions must be checked independently. If the model aims only for a description of the experimental data, particular attention shall be given on the range of studied conditions, extrapolation beyond the conditions would likely produce unreliable data.

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